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FORMATION OF A SURFACE LAYER OF MULTICOMPONENT LEAD-SILICATE GLASSES IN HYDROGEN ON HEATING

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X-ray electron spectroscopy and thermodynamic analysis are used to investigate the sequence of chemical transformations of the elements of a surface layer of silicate glass in the system $PbO – BaO – Na_2O – Al_2O_3 – SiO_2$ under heating in a hydrogen atmosphere. The process of thermal reduction of a multicomponent lead-silicate glass in hydrogen is a multistage process of diffusion and chemical interaction of lead with hydrogen. Reduction of lead is observed, the lead atoms bound with aluminum-oxygen groupings interacting being the first to interact with hydrogen after which the lead atoms in the silicon-oxygen structural units interact with hydrogen. The remaining components of the glass do not interact with hydrogen in the temperature range 375 – 475°C. The concentration profiles of the elemental distribution in the surface layer of the reduced glasses are determined.

All modern microchannel plates are manufactured from multicomponent lead-silicate glasses containing alkali and alkali-earth metal oxides (RF patent No. 2010774). The microchannel structures are created by extruding multichannel fiber rods made of lead-silicate and soluble borate glass, sintering them into a fiber block, and etching out strands chemically with hollow channels being formed in their place (RF patent No. 2085523) [1].

The multichannel structure obtained is heat-treated in a hydrogen atmosphere, as a result of which a working layer, possessing emission properties, is formed on the inner surface. The coefficient of secondary electron emission is an additive function of the composition of the surface layer. It is known that when the surface layer is enriched with silicon and barium oxides and depleted of lead and sodium oxides the emission properties of the glass improve [2]. The concentration of lead reduced to metal determines the surface resistivity: the minima of the resistance approximately correspond to the maxima of the highest value of the coefficient of secondary electron emission [2].

Since both factors, which act to make the reduced glass usable for manufacturing microchannel plates (the surface resistivity and coefficient of secondary electron emission), are determined by the composition of the surface layers of the glasses, it is important to determine the mechanism of the formation of the composition of this layer at successive states of technological processes during the manufacturing of the microchannel plates.

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The objective of the present work is to investigate the composition of the surface layers of silicate glass from the system $PBO – BaO – Na_2O – Al_2O_3 – SiO_2$ at the state of reduction in hydrogen during heating.

Lead-silicate glass 6Ba4 with the following composition (%[2]) was investigated: 11.7 PbO, 3.9 BaO, 5.4 Al_2O_3 15.4 Na_2O, 63.5 SiO_2. This glass is used to manufacture microchannel plates.

The glass was obtained at the State Optical Institute from a mix melt in 80 cm^3 platinum crucibles in an electric furnace with Silit heaters. The glass mass was poured into metal molds and the castings were annealed in a muffle furnace. The temperature of the mix melt was 1400°C, the casting temperature was 800°C, cooling was performed at the rate 4 – 6 K/min to 500°C, and annealing was performed at 500°C for 6 h in an inert atmosphere.

The reduction of the glasses was conducted in a hydrogen atmosphere at pressure 760 mm Hg and temperatures 375, 400, 425, and 475°C over a period of 1 h.

The surface composition of the glasses was investigated with an ÉS-2401 spectrometer. The spectra were excited with MgK_α radiation. The vacuum in the chambers of the spectrometer was 1×10^{-9} and 5×10^{-10} mm Hg in the analyzer and preparatory chambers, respectively.

The thermodynamic calculations of the interaction of lead-silicate glasses with hydrogen were performed by the procedure of [3], which is based on finding the extrema of the entropy of the system while satisfying a number of boundary conditions and implemented in the ASTRA pro-

[2] Here and below — content by weight.

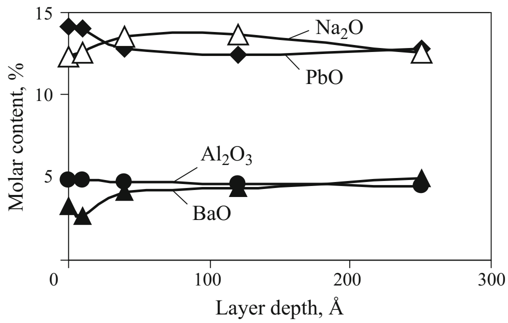

Fig. 1. Concentration distribution profiles of the elements in the surface layer of 6Ba4 glass after heat treatment in argon (1×10^{-6} mm Hg) at 400°C.

gram (whose author is B. G. Trusov, Bauman Moscow Technical School). The method which we used to perform a thermodynamic analysis of the surface layers of the glasses formed during the interaction of with hydrogen is examined in detail in [4]. The characteristics of the isothermal equilibrium and the content of the components were calculated under the following conditions in the model system PbO – BaO – Al_2O_3 – Na_2O – SiO_2 (6Ba4 glass) – gas: temperature 400°C and total pressure 760 mm Hg in the hydrogen atmosphere. The glass was represented as an ideal solid solution of crystalline compounds. The thermodynamic properties of the components of the gas and condensed phases of the system which are required to perform the thermodynamic calculations were taken from the handbook [5].

It is known that lead plays a dual functional role in the structure of silicate glasses — as a glass former and as a modifier. In a previous work [4], it was shown that the character of the bond of the glass-former is close to that in PbO_2 and that of the modifier in PbO.

X-ray electron analysis established that in the structure of the 6Ba4 glass lead is present predominately in the modifier state. The glass-former fraction is 6% of the total amount of lead, i.e., almost two times less than in the structure of dual low-lead glass (30% PbO).

To investigate the thermally stimulated processes in the surface layers, the glass samples were heat-treated in an inert argon atmosphere in the vacuum chamber of the ÉS-3201 spectrometer at temperature 400°C. The argon pressure was 1×10^{-6} mm Hg.

X-ray electron analysis showed that the following are observed as a result of the heat-treatment:

negligible sodium and lead depletion of the glass surface;

decrease of the lead-grass-former fraction (to trace amounts);

decrease of the barium content in the about 50 Å outer surface layer, while the concentrations of Al_2O_3, and PbO remain practically constant in a 250 Å thick layer.

Figure 1 shows the concentration distribution profiles of the elements in the surface layer of the glass after heat treatment.

The system model glass – argon under isothermal conditions at 400°C was analyzed for the thermodynamic analysis of thermally stimulated processes. In this case, PbO_2 decomposes with PbO forming and oxygen being released, and PbO passes into the gas phase in the form of PbO monomers and Pb_2O_2 dimers. Sodium also passes into the gas phase.

The main components of the gas phase are in the ratio $[Pb^0] : [PbO] : [Na] : [Pb_2O_2] = 100 : 10 : 1 : 10^{-3}$.

The thermally stimulated redistribution of the elements in the surface layer of multicomponent lead-silicate glasses has been investigated in [6]. The procedure proposed by F. Z. Gil'mutdinov in [7] was used to analyze the thermally stimulated changes of the composition. This procedure is based on the following:

searching for a relation between the type of phase diagrams and the composition of the surface layer;

the known correlation between the surface energy and the melting temperature;

a method for simulating multicomponent systems by a collection of binary systems; this method is widely used in thermodynamics and statistical physics.

The procedure consists in analyzing the phase diagrams of binary systems which are composed of the components of the system under study. The composition changes in the direction of the closest minima on the liquidus curves, i.e., a composition with the lowest melting temperature forms in the surface layer. The system under study is represented in the form of binary systems composed of pairs of components. The phase diagrams of these systems are analyzed in the following sequence. First, the elements that segregate toward the surface are determined from the phase diagrams of the main (alloying) element; the melting temperature of these elements characteristically decreases as their concentration increases in this system. Next, the diagrams of phases which consist of pairs of alloying elements are examined. When investigating diffusion processes in multicomponent oxide melts, they are treated as pseudobinary (quasibinary) systems of oxides. Consequently, the SiO_2 – MO phase diagrams were chosen to predict the thermally stimulated changes of silicate glasses.

The change in the surface composition of 6Ba4 glass can be predicted by analyzing the quasibinary phase diagrams SiO_2 – Al_2O_3 ($[Al_2O_3] : [SiO_2] = 4.7 : 95.3$), SiO_2 – Na_2O ($[Na_2O] : [SiO_2] = 19.5 : 80.5$), and SiO_2 – PbO ($[PbO] : [SiO_2] = 15.5 : 84.5$) [8]. The region with low barium content is not described in the SiO_2 – BaO phase diagram, so that the change of the barium content on the surface was not predicted. The minima on the liquidus curves in the PbO – SiO_2, SiO_2 – Na_2O, and SiO_2 – Al_2O_3 phase diagrams lie in the region 6% PbO, 20% Na_2O, and 5% Al_2O_3. Consequently, the lead content of surface layer should be expected to decrease.

According to the x-ray electronic data, the following characteristic processes are observed in an interaction with hydrogen: reduction of part of the oxidized lead to metal and

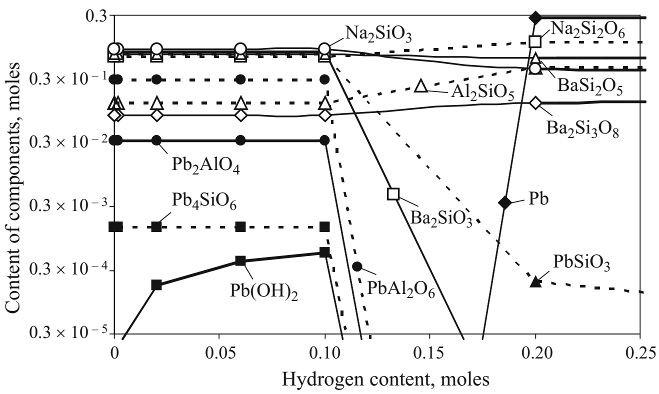

Fig. 2. Content of condensed components in the system glass (composition 11.7% PbO, 3.9% BaO, 5.4% Al_2O_3, 15.4% Na_2o, and 63.5% SiO_2) — hydrogen at 400°C (thermodynamic modeling).

formation of lead hydroxide. Ba and Na do not interact with hydrogen in the experimental temperature range.

The results of the thermodynamic analysis (Fig. 2) confirm that only lead interacts with hydrogen in the temperature interval 375 – 475°C. In contrast to the system $PbO – SiO_2$, metallic lead forms as a result of a reaction without an intermediate stage where hydroxyl groups bound with lead are formed.

At the beginning of the process lead atoms which are bound with the aluminum-oxygen groupings interact with hydrogen, and then hydrogen atoms in the silicon-oxygen structural units interact with lead.

The activation energy of the total (thermally stimulated and chemical) process of the reduction of lead in the surface layer of 6Ba4 glass is comparable to the activation energy of this process in the surface layer of the binary glass MKO20 — 26 and 18 kJ/mole, respectively.

Figure 3 displays the concentration profiles of the elements in the surface layers of the glasses which undergo reduction at different temperatures.

As compared with the initial 6Ba4 glass, the surface layers of the reduced glasses are depleted of lead and sodium oxides and enriched with barium and metallic lead oxides. It is known that the enrichment of the surface layer with silicon and barium oxides and depletion of lead and sodium oxides is accompanied by an improvement of the emission properties of the glass [2]. Analysis of the concentration profiles shows that higher values of the coefficient of secondary electron emission are to be expected for glasses reduced at 425 and 475°C than for glasses reduced at lower temperatures.

In summary, the process of thermal reduction of a multicomponent lead-silicate glass in the system PbO – BaO – Al_2O_3 – Na_2O – SiO_2 in hydrogen is a multistage process of diffusion and chemical interaction of lead with hydrogen. Reduction of lead is observed. First lead atoms bound with aluminum-oxygen groupings interact with hydrogen and then atoms of lead which are part of the silicon-oxygen structural units interact with hydrogen. The remaining components of the glass do not interact with hydrogen in the temperature range 375 – 475°C.

The activation energy of the total process of reduction of lead in the surface layer of 6Ba4 glass is approximately 26 kJ/mole.

The results obtained make it possible to determine the optimal regime for the reduction of glasses in the system

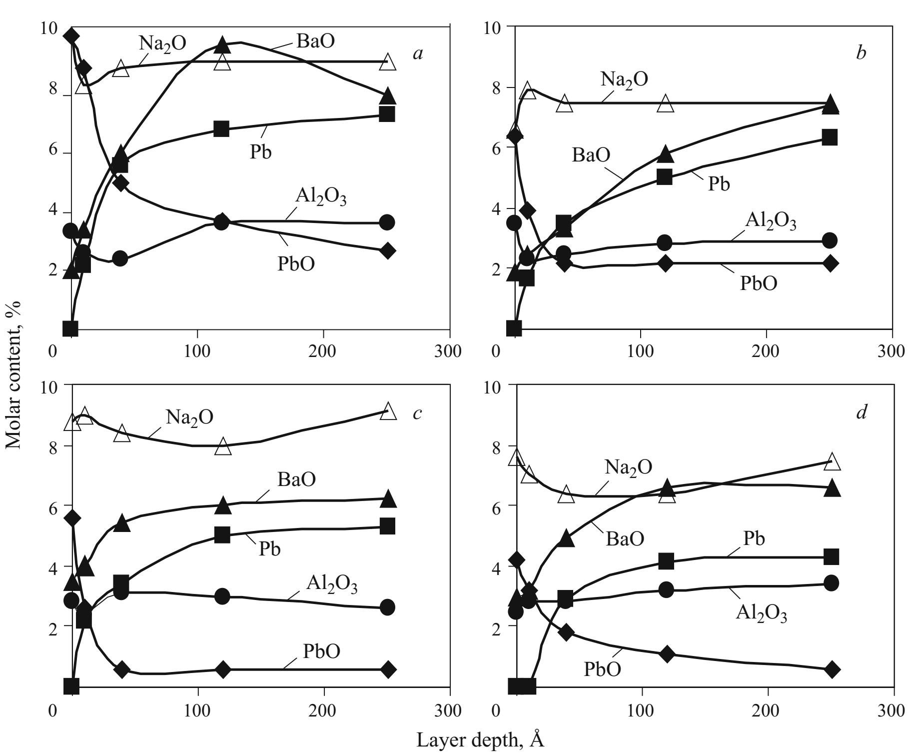

Fig. 3. Concentration distribution profiles of the elements in the surface layers of the reduced glasses at temperatures 375 (*a*), 400 (*b*), 425 (*c*), and 475°C (*d*).

$PbO – BaO – Al_2O_3 – Na_2O – SiO_2$ for manufacturing microchannel plates.

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